Reports

Iridium Profile for 10 Million Years Across the Cretaceous-Tertiary Boundary at Gubbio (Italy)

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The iridium anomaly at the Cretaceous-Tertiary (KT) boundary was discovered in the pelagic limestone sequence at Gubbio on the basis of 12 samples analyzed by neutron activation analysis (NAA) and was interpreted as indicating impact of a large extraterrestrial object at exactly the time of the KT mass extinction. Continuing controversy over the shape of the Ir profile at the Gubbio KT boundary and its interpretation called for a more detailed follow-up study. Analysis of a 57-meter-thick, 10-million-year-old part of the Gubbio sequence using improved NAA techniques revealed that there is only one Ir anomaly at the KT boundary, but this anomaly shows an intricate fine structure, the origin of which cannot yet be entirely explained. The KT Ir anomaly peaks in a 1-centimeter-thick clay layer, where the average Ir concentration is 3000 parts per trillion (ppt); this peak is flanked by tails with Ir concentrations of 20 to 80 ppt that rise above a background of 12 to 13 ppt. The fine structure of the tails is probably due in part to lateral reworking, diffusion, burrowing, and perhaps Milankovitch cyclicity.

The UPPER CRETACEOUS-PALEOCENE Scaglia Rossa formation, with an informal type section in the Bottaccione Gorge at Gubbio ($43^{\circ}22'$ N, $12^{\circ}35'$ E), is a pink pelagic limestone with 5 to 15% clay content (1-4). This limestone represents essentially continuous deposition in a deepwater environment at a (compacted) sedimentation rate of about 10 m per million years (Myr) in the Maastrichtian and 3 m per Myr in the Paleocene (2), and there are no detectable hiatuses. An Ir anomaly at the Cretaceous-Tertiary (KT) boundary there, discovered in 1978 (5), was interpreted as evidence for a major impact on the earth (6).

Subsequently this interpretation has been disputed, and two studies have suggested that there are multiple Ir peaks (7, 8). To resolve this dispute, we have studied the fine structure of the Ir anomaly. We collected samples from limestone beds at a spacing of about 5 to 10 cm, avoiding at least the larger clay seams, which may be atypical either because of diagenetic dissolution (4) or because the clay minerals may have a different source (9). We analyzed the samples using improved methods of neutron activation analysis (NAA) in which the Ir was extracted with hot iron pellets (10) or measured with a specially developed Ir coincidence counter (11).

An Ir profile over the 57-m interval from 305.10 to 362.04 m (Fig. 1) was measured to test the frequency of Ir anomalies; Ir data are reported as mass fractions of the whole rock. In this interval, representing 10 Myr (71.5 to 61.5 million years ago, Ma) (12, 13), we found no Ir concentration above background levels other than the KT anomaly. We thus strengthen the conclusion of other Ir analysts (14) that Ir anomalies are not common in the stratigraphic record.

The presence of Ir tails above and below the 3000-ppt Ir concentration in the KT clay (6) was confirmed by Crocket et al. (8) and Rocchia et al. (15). Our data (Fig. 2) reveal several details within the Ir tails. Although the Ir concentration in the tails (20 to 80 ppt) is lower than in the boundary clay (\sim 3000 ppt), the tails are thicker, and the column density in the two tails together is about three times the column density in the boundary clay. Column densities of excess Ir in limestone above and below the boundary clay are 12 ± 3 and 5 ± 1 ng/cm², respectively; in the boundary clay itself the column density is 6 ng/cm² (the main uncertainty in the clay value is the thickness of the bed). A longstanding question is whether these Ir tails provide an accurate record of the primary sedimentation history of Ir-rich material or whether they represent redistribution of Ir out of an original, sharply defined peak.

In order to investigate the geochemical fine structure of the KT Ir boundary region, Fe, Al, and Si were measured by x-ray





fluorescence and Ir with the coincidence counter (Fig. 3); Al is used as a proxy parameter for clay content. An unexpected discovery was that within the tails the whole-rock Ir profile fluctuates in a series of peaks and troughs that differ in amplitude by a factor of 2 to 5. Sample spacing is sufficiently close to show that the peaks are real.

Crocket et al. (8) reported four subsidiary Ir peaks, which they attributed to volcanic events, in clay layers at +1.1, +0.56, -1.0, and -1.8 m with respect to the Gubbio KT boundary. On a comparable carbonate-free basis, our Ir measurements from limestone beds adjacent to these clay layers are systematically lower. There are also distinct differences in the measurements of the prominent clay bed at -1.8 m; Crocket et al. obtained carbonate-free Ir values of 1000 ± 260 ppt $(\pm 1 \text{ SD})$ at Bottaccione and 2600 \pm 1000 ppt at nearby Contessa; our values are 218 \pm 18 ppt and 230 \pm 62 ppt. This analytical disagreement should be resolved by a current blind-analysis program supervised by R. N. Ginsburg of the University of Miami.

Our minor Ir peaks and troughs for limestone whole-rock samples are rhythmic and define an envelope that tails out to background (Fig. 3A). This is also true of the Ir/Al ratio, a proxy for the Ir/clay ratio (Fig. 3A) and a parameter that removes the effect of variations in CaCO₃ content. Iridium

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peaks resulting from separate events should be arhythmic and stand out above the general curve of the shoulder region. This is not the case; apparently all the excess Ir originally entered the environment during a single, large event-which many additional lines of evidence indicate was an impact (16, 17)-at precisely the time of the KT extinction. If multiple impacts occurred (17, 18), they are not stratigraphically resolvable.

Incorporation of KT-impact Ir into the upward tail may result from (i) fluvial transport into the sea of Ir that originally fell on the continents; (ii) local reworking; or (iii) bioturbation, but the presence of a similar tail in the Ir/Al ratio indicates that Ir was decoupled from and enhanced over the clay content during this remobilization.

The Ir tail below the boundary suggests that diffusion or bioturbation occurred. A 30-cm bleached zone immediately below the boundary (Fig. 2), in which Fe has been reduced and removed (19), argues for diffusion in this region immediately after the KT impact. Abundant Zoophycos (Fig. 2) and Planolites burrows demonstrate that some bioturbation occurred; Kotake (20) has shown that Zoophycos carries surface sediment downward.

The minor peaks in the Ir profile are partly suppressed on the Ir/Al curve (Fig. 3A), which suggests that the unidentified Ir carrier is in part associated with the detrital clay component; fluctuations in the Ir abundance largely reflect opposite-sign fluctuations in the CaCO₃ content. Bedding-plane dissolution (4) is rejected as a cause of lowered CaCO₃ and increased Ir because the Ir peaks do not match six major layers where solution of bedding is prominent (Fig. 2). The rhythmic Ir peaks may reflect oscillations in the clay-to-carbonate ratio of the sediment (seen in the Al and Si profiles of Fig. 3B) driven by Milankovitch cycles, but closer sampling will be needed to confirm these oscillations. Clay variations in the middle and Upper Cretaceous of the Gubbio region have been attributed to Milankovitch oscillations (21), and Milankovitch precession rhythms in the KT boundary interval have been found in the South Atlantic (22) and in Spain (23).

At Gubbio, polarity chron 29R, representing an interval evaluated at 0.44 Myr

350

m



Fig. 3. Iridium-anomaly interval in the Bottaccione section. (A) Profiles of Ir (in parts per trillion) and Ir/Al ratio $(10^{-10} \text{ g Ir per gram of})$ Al; this parameter is a proxy for the Ir-to-clay ratio) in limestone samples. (**B**) Profiles of Fe, Al, and Si (in weight percent).

(24), 0.53 Myr (25), or 0.57 Myr (13), contains an estimated 20 clay-carbonate cycles (some elided by pressure solution between 348 and 350 m); the roughly 22,000to 28,000-year period is comparable to or slightly longer than the duration of the Milankovitch precession cycle. We have some doubts over the notion that Milankovitch forcing produced the oscillations, because the reduced sedimentation rate above the KT boundary, based on the inference that the clay-carbonate cycles provide a Milankovitch clock, is not reflected in an increased Ir background level outside the anomaly interval. If Milankovitch cycles (or some other steady cycles, regardless of origin) do occur in several KT boundary sections around the world, it should eventually be possible to obtain a precise event chronology across the boundary.

REFERENCES AND NOTES

- 1. H. P. Luterbacher and I. Premoli Silva, Riv. Ital. Paleontol. Stratigr. 68, 253 (1962). M. A. Arthur and A. G. Fischer, Geol. Soc. Am.
- Bull. 88, 367 (1977).
- W. Alvarez, Geol. Soc. Am. Bull. 88, 383 (1977). _____, R. Colacicchi, A. Montanari, J. Sediment. Petrol. 55, 720 (1985). 4
- W. Alvarez et al., Eos 60, 734 (1979) 5.
- L. W. Alvarcz et al., Science 208, 1095 (1980).
 F. C. Wezel et al., C. R. Acad. Sci. Paris 293, 837 (1981); R. Vannucci, S. Vannucci, A. Mazzucotelli,



Fig. 2. (Left) Field drawing of KT boundary interval in Bottaccione section at Gubbio; bedding is rotated to horizontal. (Right) High-precision Ir values (for errors, see Fig. 1). Arrows on the right indicate the locations of solution-bedding seams.

S. Meloni, M. Oddone, Rendiconti Soc. Italiana Mineral. Petrol. 38, 413 (1982). J. H. Crocket et al., Geology 16, 77 (1988). M. J. Johnsson and R. C. Reynolds, J. Sediment.

- 8
- 9. Petrol. 56, 501 (1986).
- 10. H. V. Michel, F. Asaro, W. Alvarez, L. W. Alvarez, Init. Rep. Deep-Sea Drilling Proj. 86, 533 (1985).
- 11. L. W. Alvarez, in Book of Abstracts of the 196th American Chemical Society National Meeting, Los Angeles, CA, 25 to 30 September 1988 (American Chemical Society, Washington, DC, 1988), p. NUCL-30; H. V. Michel et al., Proc. Ocean Drilling Prog. Scientific Results 113, 159 (1990).
 12. D. V. Kent and F. M. Gradstein, Geol. Soc. Am.
- Bull. 96, 1419 (1985).
- W. A. Berggren *et al.*, *ibid.*, p. 1407.
 F. T. Kyte and J. T. Wasson, *Science* 232, 1225 (1986); C. J. Orth, J. D. Knight, L. R. Quintana, J. S. Gilmore, A. R. Palmer, *ibid.* 223, 163 (1984).
- 15. R. Rocchia et al., Earth Planet. Sci. Lett. 99, 206 (1990).
- W. Alvarez, Eos 67, 649 (1986); V. L. Sharpton and P. D. Ward, Eds., Geol. Soc. Am. Spec. Pap. 247 (in press)
- 17. W. Alvarez and F. Asaro, Sci. Am. 263, 78 (1990).
- 18. J. Smit and G. T. Klaver, Terra Abs. 1, 421 (1989). 19. W. Lowrie, W. Alvarez, F. Asaro, Earth Planet. Sci.
- Lett. 98, 303 (1990) 20. N. Kotake, Lethaia 22, 327 (1989).

- 21. W. Schwarzacher and A. G. Fischer, in Cyclic and Event Stratification, G. Einsele and A. Seilacher, Eds. (Springer-Verlag, Berlin, 1982), pp. 72–95; W. Schwarzacher, Paleoceanography 2, 79 (1987). T. D. Herbert, R. F. Stallard, A. G. Fischer, ibid. 1, 495 (1986); A. G. Fischer and T. Herbert, Soc. Geol. Ital. Mem. 31, 45 (1986); T. D. Herbert and A. G.
 Fischer, Nature 321, 739 (1986); M. E. Tornaghi,
 I. Premoli Silva, M. Ripepe, Riv. Ital. Paleontol. Stratigr. 95, 223 (1989).
- T. D. Herbert and S. L. D'Hondt, Earth Planet. Sci. 22. Lett. 99, 263 (1990).
- 23 J. Smit, personal communication.
- W. Lowrie and W. Alvarez, Geology 9, 392 (1981). 24. W. B. Harland et al., A Geologic Time Scale (Cam-25. bridge University Press, Cambridge, U.K., 1982), p. 131.
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Kinematics of Late Paleozoic Continental Collision Between Laurentia and Gondwana

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In the Appalachians, late Paleozoic Alleghanian orogenesis is widely regarded as resulting from dextral oblique collision between irregular margins of Gondwana and Laurentia. However, this relative plate motion cannot account for coeval convergence in the Ouachitas and Variscides and is incompatible with some tectonic transport indicators in the Appalachians. An alternative kinematic model is proposed in which early sinistral transpression in the Appalachians is followed by counterclockwise rotation of Gondwana and the development of a system of dextral strike-slip faults extending from southern Europe to Alabama.

HE SUPER CONTINENT OF PANGEA formed during the late Paleozoic when Gondwana (which included South America and Africa) collided with North America (Laurentia) and Europe (1). The orogenic activity resulting from this collision is referred to as the Variscan and Hercynian orogenies in Europe and as Alleghanian orogeny in the Appalachian mountains of eastern North America. The Ouachita orogenic belt, along the southern margin of North America, also formed as a consequence of the above collision. A series of Carboniferous and Permian foreland basins (Fig. 1) related to crustal loading of the continental margin by advancing thrust sheets (2) formed on North America. Salients and recesses in the orogen are at least

in part a consequence of collision of mismatched continental margins (3). A series of dextral strike-slip faults extends from southern Europe to Alabama (4-11) along the axis of the late Paleozoic orogen. Convergent motion between Gondwana and North America ceased before the end of the Paleozoic, and by Late Triassic, the continents had begun to separate, a process that eventually led to the opening of the present Atlantic Ocean (12).

There is widespread agreement among workers in the Appalachians and Ouachitas concerning most aspects of the scenario outlined in the preceding paragraph. However, there is uncertainty concerning the kinematic significance of the dextral strikeslip faulting in the internal parts of the orogen. Some workers (13) have interpreted the strike-slip faults to be a consequence of the operation of indentor or escape tectonic processes related to the convergence of mismatched continental margins. If this were the case, one would expect sinistral and dextral faults to be equally abundant. It is

difficult to account for the preponderance of dextral faults in connection with this interpretation. Other workers (14) have suggested that overall dextral-oblique convergence occurred between Gondwana and North America in the Appalachian region, and that displacement was coevally partitioned between thrust and dextral strike-slip faults. In this model, it is difficult to account for convergence along east or southeast trending segments of the orogen. One expects that dextral motion along northeast trending faults in the Appalachians would result in opening in the Ouachitas and perhaps in Europe. In this report, we propose a kinematic model that resolves the above contradictions. Discussion of this model follows an evaluation of relevant structural and geochronological data.

Rocks in the eastern Appalachian Piedmont of South Carolina and Georgia (Fig. 1) record three kinematically distinct phases of late Paleozoic deformation that are coeval with and considered to be a part of the Alleghanian orogeny observed in the Appalachian foreland (15-17). The earliest phase of Alleghanian deformation, called regional D₂ by Secor et al. (15), occurred along the Modoc fault, a 2- to 4-km-thick zone of mylonitic rocks that now dip steeply to the northwest and extend along the Fall Line in South Carolina and Georgia. The fault zone contains numerous map-scale sheets of synkinematically emplaced granitic orthogneiss and juxtaposes high-grade sillimanite-bearing schist and paragneiss of the Kiokee belt in the footwall against low-grade rocks of the Carolina slate belt in the hanging wall. Our evaluation of shear criteria in the mylonitic rocks indicates that, in its present orientation, the Modoc fault accommodated oblique-slip with dextral and normal components of at least 18 and 4 km, respectively (18). However, the present orientation of the fault is a consequence of F_3 folding (15). Regional geologic relationships (Fig. 1) (18, 19), seismic reflection data (20), and structural analysis of the D₃ Kiokee antiform (21) indicate that the Modoc fault originally had a low angle of dip. Recent ⁴⁰Ar/³⁹Ar geochronological data (22) and geothermobarometry calculations (23) suggest that as much as 15 km of crust has been omitted across the fault. We interpret the D₂ Modoc fault to be a low-angle normal fault associated with southward delamination of oceanic lithosphere from continental lithosphere at the onset of the Alleghanian orogeny (24) (Fig. 2).

Between 295 and 285 million years ago (Ma; during D3) the Modoc fault zone was deformed by the development of northeasttrending, northwest-vergent folds (15–17, 21). These folds are interpreted to represent

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